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# Solid-state photochemistry of molecular, photo-switchable species: the role of photocrystallographic techniques

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**Synopsis** The analysis of the structures of metastable linkage isomers, generated photochemically, using single-crystal photocrystallographic techniques is described. The factors that favour the formation of the metastable states are discussed.

**Abstract** Over the last 30 years the single crystal photocrystallographic technique has been developed to determine the three-dimensional crystal and molecular structures of metastable species which have been generated in the crystal photochemically. Transition metal complexes that have been investigated using this methodology include complexes that contain nitrosyl, dinitrogen, sulfur dioxide and nitrite ligands, all of which form new linkage isomers in the solid-state when photoactivated by light of the appropriate wavelength. Both steric and electronic factors determine the level of the conversion from the ground state structure to the metastable isomeric structure, and both the “reaction cavity” size and the nature of the intermolecular interactions are shown to be among the key factors that influence the percentage conversion.

## 1. Introduction

Since the technique was first developed a century ago (Bragg & Bragg, 1913), for many decades X-ray crystallography had been thought limited to providing information that is both space-averaged over all of the molecules in the crystal and time-averaged over the period of the diffraction experiment. With the rapid progression of X-ray methods it became evident that the crystal was not, as previously believed, a static array of rigid molecules (Dunitz *et al.*, 1988). It has been shown that a considerable amount of movement can occur within the lattice, with atomic vibrations, dynamic disorder and even complete chemical reactions possible without the loss of single crystal integrity. Today, the structural study of single-crystal-to-single-crystal transformations is conducted using increasingly routine methods, with excitation achieved via a range of different stimuli including temperature, pressure, magnetism and light.

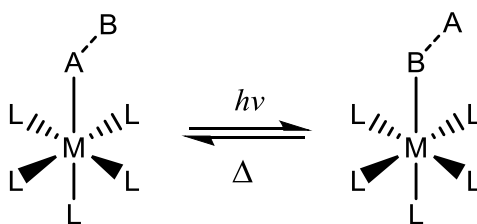
Photochemically-induced changes in small, molecular species continue to be of particular interest in a number of research areas. Light is an attractive choice of excitation stimulus for many applications as photochemical reactions can be highly efficient, site-specific and flexible, with reaction conditions easily optimised by tuning the excitation source across the spectral range. Some of the earliest comprehensive photochemical studies were conducted with organic species in the late 19<sup>th</sup> and early 20<sup>th</sup> centuries (Roth, 1989). Since this time, photochemical reactions in solution have been investigated extensively and, as such, many details of these processes are now well understood. However, the study of light-induced changes in solid-state samples is less established. Solid-state photoactive materials are of particular importance for their potential application to a number of real world challenges (Zhang *et al.*, 2013). These range from the development of new technologies, including solid-state sensors, optoelectronic devices and ultra-high capacity data storage media to environmental and biomedical applications. The first extensive investigation of photoinduced changes in the solid-state was conducted by Cohen and Schmidt in 1964. Their study of irreversible [2+2] photodimerisations in a selection of *trans*-cinnamic acids by X-ray diffraction, led to the proposal that solid-state photochemical reactions proceed “topotactically”. Their Topochemical Postulate (Cohen & Schmidt, 1964) proposes that restrictions imposed by the crystal lattice ensure that the reaction will follow a minimum energy pathway, undergoing the least amount of atomic movement possible in order to preserve the crystalline environment. Since this time, the development of modern structural chemistry has helped to advance our understanding of solid-state photoreactions. While Cohen and Schmidt were limited to studying only initial states by crystallography, technological improvements, including advances in computing power, cryogenic technologies (Goeta & Howard, 2004) and the increasing availability of high-flux X-ray sources (Clegg, 2000; Neutze & Moffat, 2012), have since allowed the study of photoinduced products by X-ray methods. As a result, since the 1990s the term “photocrystallography” has become widely used to describe this rapidly emerging research area (Coppens, 2009).

While extensive study of irreversible processes, including [2+2] photodimerisation reactions (Natarajan & Bhogala, 2011; Elacqua *et al.*, 2012), has continued since the 1960s, much work in the field has also aimed to identify solid-state systems that undergo reversible changes on photoactivation. Examples include spin-crossover complexes that display Light-Induced Excited Spin-State Trapping (LIESST) behaviour (Halcrow, 2009; Thompson *et al.*, 2005), photo-induced metal – metal bond length changes (Kim Christopher *et al.*, 2002; Coppens *et al.*, 2004) and solid-state linkage isomerism. For many real-world applications, the ability to reversibly convert between

two different, controllable states is imperative for a potential functional material. It is therefore unsurprising that a considerable volume of work has been dedicated to the study of these “photoswitchable” species in their technologically applicable solid-state. This review outlines the integral role structural chemistry has to play in this research, emphasising the necessity of combining photocrystallographic data with the results of spectroscopic and computational experiments to reveal a complete, 3D picture of the changes that occur. The discussion is illustrated with examples of photocrystallographic studies involving linkage isomers, a diverse range of molecular species that have been shown to possess highly interesting photoswitchable capabilities.

## 2. Solid-state linkage isomerism

The ability of a small, ambidentate ligand to bind to a transition metal centre through its different possible donor atoms generates related, though structurally distinct molecules known as linkage isomers (Jørgensen, 1894). While the earliest linkage isomer species were prepared by changing the reaction conditions to favour a particular coordination mode (Adell, 1944), conversion between isomers can also be induced on excitation by an external stimulus, *e.g.* light or heat. When the ambidentate ligand is small and the changes involved in the isomerisation are relatively modest, the process can be induced in the solid-state. In the majority of systems, photoconversion to a metastable linkage isomer can be achieved by irradiation at cryogenic temperatures, with the reverse process induced on warming the system above a threshold temperature known as the metastable limit (Figure 1). These metastable isomers are ideal for steady-state photocrystallographic experiments, as the atomic rearrangements involved are sufficient to produce a change in the X-ray diffraction pattern, but at the same time are gentle enough that the crystallinity of the sample can be preserved.

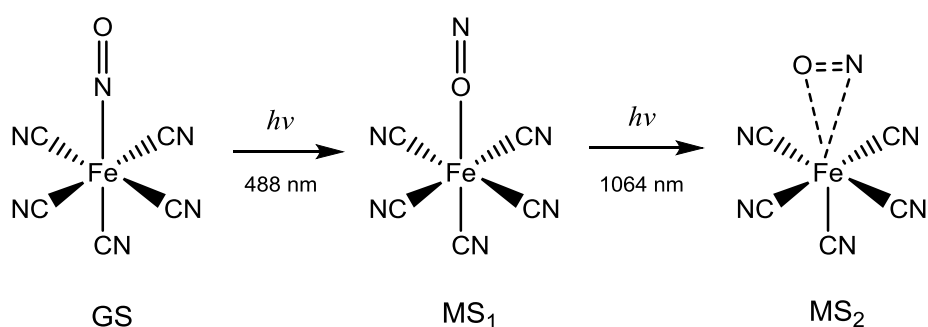


**Figure 1** Schematic representation of photochemical linkage isomer conversion, M = metal centre, AB = isomerisable ligand, L = ancillary ligand.

## 3. Nitrosyl linkage isomers

The first observation of solid-state conversion between two linkage isomer species was made on the iron – nitrosyl complex sodium nitroprusside, SNP. Early investigations of the compound using

Mössbauer spectroscopy had identified the presence of two, unexpectedly long-lived photoactivated species (Hauser *et al.*, 1977). The excited states were metastable only on irradiation at low temperatures and were assigned the labels MS<sub>1</sub> and MS<sub>2</sub>. Despite further spectroscopic studies (Zöllner *et al.*, 1989; Rüdinger *et al.*, 1991), a satisfactory explanation for the unusual stability of MS<sub>1</sub> and MS<sub>2</sub> could not be provided until a photocrystallographic study conducted by the Coppens group in 1997 (Carducci *et al.*, 1997). They determined that photoexcitation in the system manifests itself as a change in NO coordination (Figure 2). Irradiation of a single crystal with 488 nm light, at 50 K, induced 37% conversion from a ( $\eta^1$ -NO) ground state (GS) arrangement to an ( $\eta^1$ -ON) linkage isomer, MS<sub>1</sub>. This atomic rearrangement was identified from the observation that the anisotropic displacement parameters for the nitrogen and oxygen atoms in the photoactivated data became more physically acceptable when the atom positions were reversed to give the isonitrosyl form. This same, photoactivated crystal was then subjected to irradiation at  $\lambda = 1064$  nm, and a subsequent photocrystallographic dataset revealed that MS<sub>1</sub> had been converted into a side-on bound ( $\eta^2$ -NO) isomer. This arrangement was assigned as the second metastable state, MS<sub>2</sub>, and could be detected at 10% occupancy. Complimentary computational studies were also conducted to explore the complicated interplay between the GS, MS<sub>1</sub> and MS<sub>2</sub> states. These suggested that irradiation with visible light induces initial excitation into the MS<sub>2</sub> arrangement, which is then converted into MS<sub>1</sub> on continued illumination. This helps explain the crystallographic observation of MS<sub>1</sub> with extended irradiation at  $\lambda = 488$  nm. Subsequent excitation with 1064 nm radiation is then calculated to promote depopulation of the metastable states, with MS<sub>1</sub> decaying via the MS<sub>2</sub> arrangement. The pathway suggests why only the side-on bound MS<sub>2</sub> isomer is observed with low occupancy after the crystal is exposed to this longer wavelength. Following on from this investigation, the nitroprusside anion has become a model system for the study of the photoinduced nitrosyl linkage isomerisation process, with a large volume of spectroscopic and computational work building upon the crystallographic result (Schaniel *et al.*, 2005; Schaniel & Woike, 2009; Dieckmann *et al.*, 2010; Schaniel *et al.*, 2010).

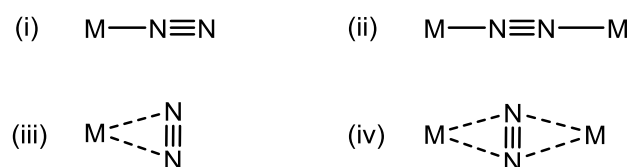


**Figure 2** Schematic representation of linkage isomerism in the nitroprusside anion; GS =  $\eta^1$ -NO nitrosyl, MS<sub>1</sub> =  $\eta^1$ -ON isonitrosyl, MS<sub>2</sub> =  $\eta^2$ -NO side-on isomer (Carducci *et al.*, 1997).

Nitric oxide is important in many biological and biochemical processes and, in particular, transition metal – nitrosyl compounds have attracted attention for their ability to release NO on excitation (Ford & Lorkovic, 2002), a property that suggests their potential as NO delivery systems for medical applications. Given this significance, it is unsurprising that nitrosyl species have been and continue to be the subject of photochemical investigation. Similar observations of metastable photoexcited states were reported for the complex  $[\text{Ni}(\text{NO})(\eta^1\text{-Cp})]$ , where  $\text{Cp} = \text{C}_5\text{H}_5^-$ , by infrared (IR) spectroscopy (Crichton & Rest, 1977). Subsequent Extended X-ray Absorption Fine Structure (EXAFS) experiments had suggested that photoexcitation was accompanied by bending in the NO unit, with the Ni–N–O angle reduced from linearity to *c.a.*  $133 - 160^\circ$  (Chen *et al.*, 1994). In light of these findings, Coppens *et al.* undertook a photocrystallographic study of the analogous  $\text{Cp}^*$  complex (Fomitchev *et al.*, 1998). At 25 K, 47% conversion to  $\text{MS}_2$  was achieved by photoactivation with 458 nm light and a Ni–N–O angle of  $92^\circ$  was determined, signalling a considerably larger rearrangement than that suggested by the earlier EXAFS result. Parallel DFT studies confirm that  $\text{MS}_2$  represents a minimum on the potential energy surface and also suggest the existence of an  $\text{MS}_1$  isomer. Photocrystallographic evidence for  $\text{MS}_1$  in this particular complex has not been reported, although bands typical of this isomer have been observed by low temperature IR spectroscopy (Schaiquevich *et al.*, 2000). Single crystal studies of a number of other photoactive NO systems, including ruthenium and heme systems, have been conducted by the Coppens group and a summary of this work is given in their own comprehensive review (Coppens *et al.*, 2002). Additionally, structural and spectroscopic studies are recently reported for a selection of cationic ruthenium – nitrosyl species, investigating the influence different anions can have on the NO rearrangement (Cormary *et al.*, 2012).

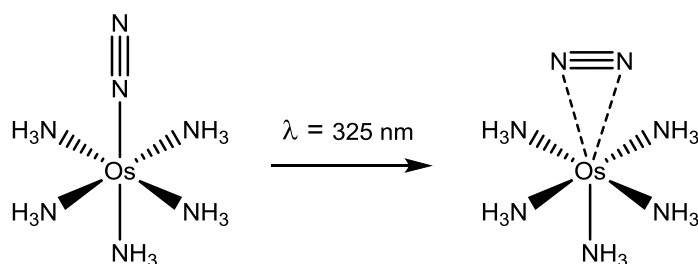
#### 4. Dinitrogen linkage isomers

Another biologically important molecule, dinitrogen, is known to display linkage isomerism behaviour. Although generally considered to be inert,  $\text{N}_2$  was first observed to act as a ligand in 1965, forming the cationic ruthenium species  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$  (Allen & Senoff, 1965). This discovery sparked great interest in the coordination chemistry of  $\text{N}_2$  in the late 1960s and 1970s, with complexes investigated via a range of techniques including NMR and IR (Bercaw *et al.*, 1974), ESR (Gynane *et al.*, 1978) and, in a few cases, by single crystal X-ray diffraction (Jonas *et al.*, 1976). Through this body of work it was revealed that  $\text{N}_2$  is capable of binding in several different coordination modes (Figure 3), broadly categorised as either “end-on” (Chatt *et al.*, 1971; Chatt & Leigh, 1972) in a (i) terminal or (ii) bridging arrangement, or “side-on” (Jonas *et al.*, 1976; Gynane *et al.*, 1978), again being (iii) terminal or (iv) bridged.



**Figure 3** Schematic representation of possible  $N_2$  coordination modes (Jonas *et al.*, 1976).

The first photocrystallographic study to investigate the potential for photoconversion between  $N_2$  isomers in the solid-state was conducted by the Coppens group on the system  $[Os(NH_3)_5(N_2)](PF_6)_2$  (Fomitchev *et al.*, 2000), an osmium analogue of the original ruthenium –  $N_2$  cation discovered by Allen and Senoff. This study provided the first undisputed structural determination of the side-on  $\eta^2$ - $N_2$  ligand coordinated terminally to a single metal centre (Figure 3(iii)), produced photochemically by isomerisation from the GS end-on arrangement (Figure 3(i)). A metastable species was induced on photoactivation with a He/Cd laser, at  $\lambda = 325$  nm and 100 K, with an occupancy of 17.4% refined from the X-ray data. This conversion level was sufficient to identify significant changes in the Os–N–N angle, Os–N and N–N bond distances, confirming the production of the  $\eta^2$ - $N_2$  linkage isomer. The photocrystallographic data are supported by complimentary low temperature solid-state IR and differential scanning calorimetry (DSC) experiments. These spectroscopic results compare qualitatively with the crystallographic data and, in addition, parallel DFT calculations predict similar geometry changes to those observed by experiment.

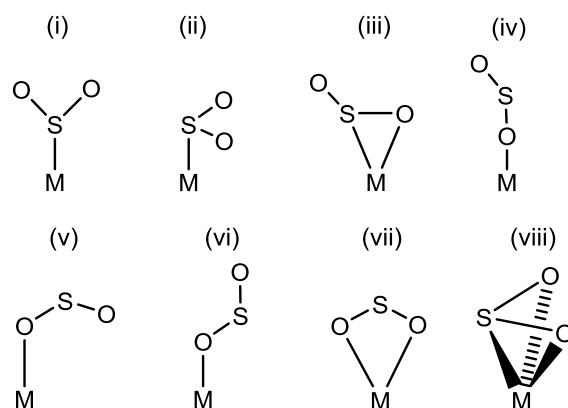


**Figure 4** GS “end-on”  $\eta^1$ - $N_2$  and metastable “side-on”  $\eta^2$ - $N_2$  linkage isomers in the  $[Os(NH_3)_5(N_2)]^{2+}$  cation (Fomitchev *et al.*, 2000).

## 5. Sulfur dioxide linkage isomers

One of the advantages of applying linkage isomer species to the rational design of potential solid-state devices is the diverse range of ambidentate ligands shown to display the phenomenon. As well as the diatomic ligands already discussed, linkage isomerisation can also be achieved in complexes containing triatomic photoactive ligands. Before the seminal work published in 1979 by Johnson and Dew, while a few different coordination modes for the sulphur dioxide ligand were known, no linkage

isomers had been observed. From photochemical IR experiments, the authors determined that isomerism had been induced in the complex *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>Cl(SO<sub>2</sub>)]Cl (Johnson & Dew, 1979). Changes in  $\nu(\text{SO}_2)$  were observed as a result of irradiation with 365 nm light at 195 K, which were attributed to a photoexcited metastable  $\eta^2\text{-(O,SO)}$  isomer (Figure 5(iii)). This arrangement has subsequently been assigned the label MS<sub>2</sub>, in analogy with the side-on bound nitrosyl species.



**Figure 5** Schematic representations of possible coordination modes for the sulfur dioxide ligand in a transition metal complex (Kovalevsky, Bagley & Coppens, 2002).

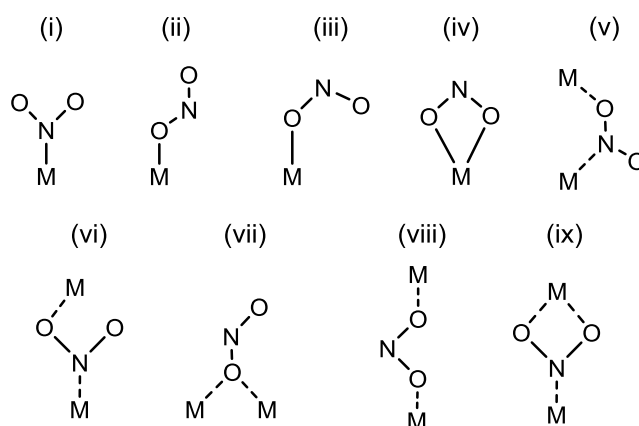
Crystallographic evidence for the  $\eta^2\text{-(O,SO)}$  isomer was not obtained until much later, when the single crystal X-ray structure for the photoactivated MS<sub>2</sub> isomer was obtained in a steady-state photocrystallographic experiment involving the same ruthenium cation (Kovalevsky, Bagley & Coppens, 2002). These crystallographic data were again confirmed by parallel IR and DSC measurements conducted in the solid-state, and similar studies were quickly completed for a small series of related ruthenium – nitrosyl compounds (Kovalevsky, Bagley, Cole *et al.*, 2002). The experiments confirm that MS<sub>2</sub> can be regularly achieved in the single crystal, by illumination at low temperature in the range  $\lambda = 300 - 500$  nm. Other sulfur dioxide linkage isomers could not be confirmed by crystallographic studies until 2006, when a bent  $\eta^1\text{-OSO}$  isomer (Figure 5(v)) was determined at 13 K for the complex [Ru(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(SO<sub>2</sub>)] [MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]<sub>2</sub>, with a photoconversion level of 36% (Bowes *et al.*, 2006). This metastable linkage isomer was assigned as MS<sub>1</sub>, being analogous to the  $\eta^1\text{-ON}$  arrangement for the nitrosyl ligand. Subsequent structural studies of sulfur dioxide species have continued to probe ruthenium complexes, with recently reported work investigating the decay behaviour of the photoinduced metastable isomers. In a photocrystallographic study of the complex tetraamineaqua(sulfur dioxide)ruthenium(II)-camphorsulfonate, photoinduced MS<sub>1</sub> and MS<sub>2</sub> isomers are observed at 100 K. From kinetic experiments conducted at 120 K, the authors suggest a decay mechanism by which the MS<sub>1</sub> population decays into the MS<sub>2</sub> arrangement (Phillips *et al.*, 2012). The authors confirm this proposed decay pathway in a second kinetic study



involving a selection of ruthenium – sulfur dioxide species  $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{X}]$ , where the *trans*-ligand X is one of a series of chloro-substituted pyridines. It is also suggested that the nature of the pyridine ligand affects the thermal stability of the MS2 isomer for this series, with a trend apparent between the rate of MS2 decay and the  $\sigma$ -donating ability of the *trans*-oriented ligand (Sylvester *et al.*, 2012). Other work has investigated the effect that the surrounding crystal lattice might have on sulfur dioxide conversion. The compounds  $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{X}](\text{tosylate})_2$ , where X = either isonicotinamide or isonicotinic acid, are found to crystallise with two chemically identical, though crystallographically distinct molecules in the asymmetric unit, which are shown to undergo different levels of photoconversion on activation. The difference in their photoisomerism behaviour is attributed to changes in intermolecular contacts between the two different crystalline environments, highlighting the important influence that steric interactions can have on the progress of a solid-state photoreaction (Sylvester & Cole, 2013b). Most recently, a transduction effect induced by sulfur dioxide isomerism has been reported to cause rotational movement further along the molecule, which it is suggested could behave as a molecular machine (Sylvester & Cole, 2013a). For this latter example, as conversion is achieved on activation with natural light, the process is suggested as a potential clean energy model.

## 6. Nitrite linkage isomers

The ambidentate nature of the nitrite ligand has been known since early studies conducted by Jørgensen (Jørgensen, 1894). The nitrite ligand is theoretically capable of adopting a wide variety of binding modes in a coordination complex (Figure 6), although the most common geometries reported have been the nitro- $(\eta^1\text{-NO}_2)$ , *endo*- and *exo*-nitrito- $(\eta^1\text{-ONO})$  and nitrito- $(\eta^2\text{-O,ON})$  isomers (Figures 6(i), (ii), (iii), (iv) respectively).



**Figure 6** Schematic diagram of the theoretically possible coordination modes for the nitrite ligand (Chattopadhyay *et al.*, 2005).

### 6.1 Photochemical nitro – nitrito isomerisation

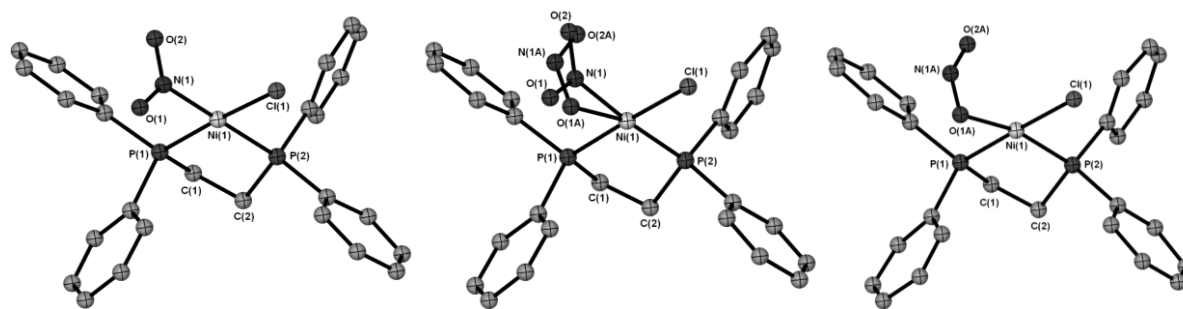
Since Jørgensen's pioneering work with the complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ , linkage isomerism in this cobalt – nitrite species has been studied comprehensively via a number of analytical techniques. The solution-state photochemistry of the cation was first reported by Adell and co-workers in 1944. They determined that, while separate nitro- ( $\eta^1\text{-NO}_2$ ) or nitrito- ( $\eta^1\text{-ONO}$ ) isomers can be selectively prepared under differing reaction conditions, conversion between GS nitro and ES nitrito forms can be photoinduced by irradiating a solution of the GS isomer under UV light (Adell, 1944). The same complex was later the subject of seminal structural experiments by Grenthe and Nordin, investigating the progress of both thermal nitrito – nitro conversion and photoactivated nitro – nitrito isomerisation, in microcrystalline powder samples by X-ray powder diffraction (Grenthe & Nordin, 1979a, b). By analysing a series of powder patterns collected at regular intervals, the authors were able to follow each rearrangement with time. The gradual shift of peak positions in successive diffractograms reflects changes in the unit cell parameters, which occur as a result of the change in nitrite coordination. As such, the level of nitro – nitrito conversion for each process could be inferred from these data.

One of the main factors that have limited the progress of structural studies investigating all solid-state linkage isomer systems has been the relatively low photoconversion level achieved in the single crystal. By the mid 2000s, maximum excitation to a metastable species was in the order of 50% conversion, a factor that affects the possible applications of such compounds. Ideally, high levels of photoactivation that are fully controllable are required if these long-lived photoexcited states are to be useful in any real-world technology.

It is possible that steric interactions from the surrounding lattice may influence the level of conversion that can be achieved in a photoactive crystal. This reasoning echoes the early work of Schmidt and Cohen suggesting that only topotactic reactions, involving minimum rearrangement at the atomic level, will occur without compromising the integrity of the crystalline sample (Cohen & Schmidt, 1964). While the practical applications of the Topochemical Postulate are largely qualitative, in later work Cohen proposed the “reaction cavity” concept as a more quantitative means of defining the changes occurring in the crystal as a result of photoactivation (Cohen, 1975). The reaction cavity, or cage, is defined as the region that encapsulates the photoactive part of the system and any necessary atomic rearrangements are assumed to occur within the cavity. The cavity walls are not confined to

be rigid, but any atomic movements are expected to exert pressure on the “cavity walls” that will lead to a distortion of the region. The size and shape of the reaction cavity can be determined easily from both the GS and photoactivated X-ray structures, allowing direct comparison. The concept has been applied by Ohashi *et al.* to rationalise the changes in single crystals of chiral cobaloxime complexes that undergo racemisation on exposure to either visible light or X-rays (Ohashi & Sasada, 1977). Extensive investigation has suggested that both the size and shape of the reaction cavity can have a marked effect on the photoactivity of the cobaloxime species. Whilst it has been shown that the rate of racemisation increases linearly with the size of the reaction cavity (Ohashi, 1988), most recently it is reported that the shape of the cavity influences the reaction pathway and can ultimately control the chirality of the photoproduct that is produced in the single crystal (Ohashi, 2013). This analysis suggests that manipulation of the reaction cavity may lead to greater control over the photoreaction and, as such, the concept is worth considering when designing new photoactive solid-state systems.

In 2009 we began photocrystallographic studies on a series of transition metal – nitrite compounds designed using simple crystal engineering principles, aiming to maximise the reaction cavity around the photoactive nitrite ligand. As part of this work the novel complex  $[\text{Ni}(\text{dppe})(\eta^1\text{-NO}_2)\text{Cl}]$ , where  $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ , was identified. It was proposed that the bulky ancillary ligand would dominate the crystal packing arrangement and, as the diphosphine group is expected to be photoinert at the excitation wavelength, the majority of the crystal should therefore remain unchanged on irradiation. Photoisomerisation in the appreciably smaller nitrite group should then be free to occur, imparting minimal steric strain to the surrounding lattice and inducing little change in the overall structure. A combination of Raman spectroscopy and photocrystallographic methods revealed that 100% nitro – nitrito isomerisation could be achieved in single crystals of the complex, providing the first reported example of 100% photoconversion in a linkage isomer system (Warren *et al.*, 2009). The GS nitro- $(\eta^1\text{-NO}_2)$  isomer was irradiated with 400 nm LED light at 100 K, *in-situ* on the diffractometer using a specifically designed set-up (Brayshaw *et al.*, 2010). After a short irradiation period of 20 min, an already strikingly high conversion level of 70% to an *endo*-nitrito- $(\eta^1\text{-ONO})$  arrangement could be determined. Further illumination for a total of 90 min was sufficient to produce a maximum, 100% conversion to the metastable *endo*-nitrito isomer (Figure 7). When the photoactivated crystal was warmed above its metastable limit, the reverse nitrito – nitro process was induced, confirming that the reaction is reversible. The related systems  $[\text{Ni}(\text{dppe})(\eta^1\text{-NO}_2)_2]$  and  $[\text{Ni}(\text{dcpe})(\eta^1\text{-NO}_2)_2]$ , where  $\text{dcpe} = 1,2\text{-bis}(\text{dicyclohexylphosphino})\text{ethane}$ , are also reported to undergo 100% conversion to a metastable *endo*-nitrito- $(\eta^1\text{-ONO})$  isomer, on irradiation at low temperature with 400 nm LED light (Warren *et al.*, 2013).

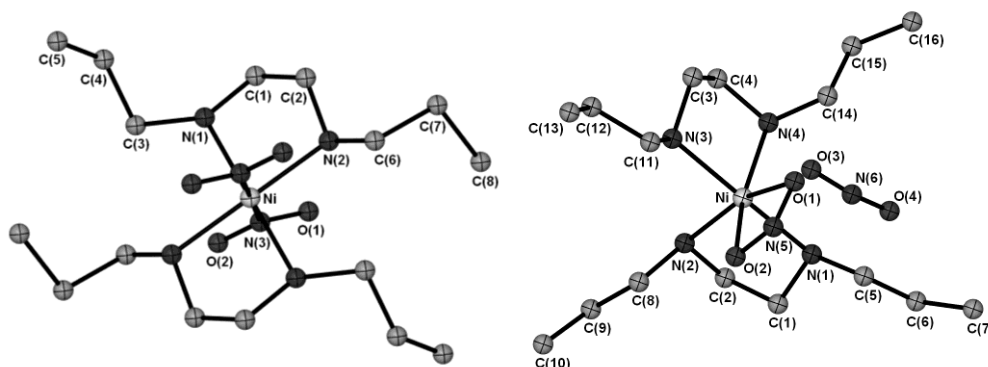


**Figure 7** Single crystal X-ray structures of  $[\text{Ni}(\text{dppe})(\text{NO}_2)]\text{Cl}$ , (left) GS, (middle) metastable arrangement after 20 min irradiation, (right) 100% *endo*-nitrito isomer after 90 min irradiation (Warren *et al.*, 2009).

## 6.2 Thermal nitro – nitrito isomerisation

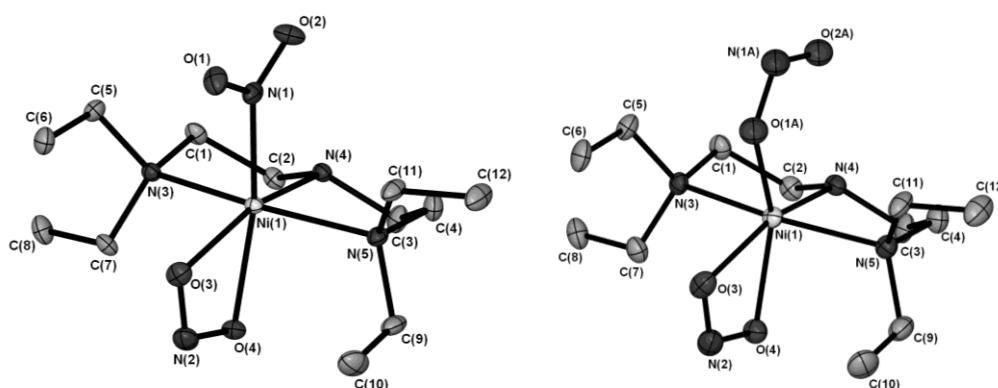
Nitro – nitrito conversion can also be promoted in the solid-state by thermal excitation. Temperature-induced linkage isomerism has mainly been observed in nickel – nitrite species of the general formula  $[\text{NiL}_2(\text{NO}_2)_2]$ , where  $L$  are  $N$ -substituted ethylenediamine ancillary ligands. Early IR and electronic spectroscopic studies, conducted in solution by Goodgame and Hitchman, suggested the preference for a particular nitrite isomer is controlled by the steric demands of the auxiliary amine group (Goodgame & Hitchman, 1964, 1966). While red solutions of nitro- $(\eta^1\text{-NO}_2)$  isomers were obtained using smaller amine ligands, blue solutions of nitrito- $(\eta^1\text{-ONO})$  complexes formed preferentially when bulkier ethylenediamines were used. Much later, structural studies by Laskar *et al.* investigated thermal isomerisation in single crystals of the complex  $[\text{Ni}(N,N'\text{-dipropyl-ethylenediamine})_2(\eta^1\text{-NO}_2)_2]$  (Laskar *et al.*, 2001). Brown crystals of the nitro- $(\eta^1\text{-NO}_2)$  form were obtained from the fresh reaction mixture, however on aging at room temperature for a few days the crystals undergo a colour change to greenish-blue. Crystallographic studies confirmed that a single-crystal-to-single-crystal transformation had occurred in which one nitro- $(\eta^1\text{-NO}_2)$  had been cleaved from the nickel centre, leaving a cationic product species containing a single nitrito- $(\eta^2\text{-O,ON})$  ligand (Figure 8). The uncoordinated nitrite group was found to remain in the crystal lattice, now acting as the counteranion for the metal cation. Conversion to the bidentate arrangement at room temperature suggests that this isomer is the more thermodynamically stable arrangement in this system, supporting Goodgame and Hitchman's proposal that the presence of bulky amine ancillary ligands will promote nitrito coordination. Laskar *et al.* report that conversion to the nitrito- $(\eta^2\text{-O,ON})$  isomer is accelerated on heating, however they do not include any high-temperature crystallographic data in support of this assertion. In addition, by storing the crystals below 10 °C the brown nitro- $(\eta^1\text{-NO}_2)$  isomer was

preserved, providing further confirmation that the linkage isomerism reaction in this complex is thermally controlled.



**Figure 8** Single crystal X-ray structures of nitro-( $\eta^1$ -NO<sub>2</sub>) GS (left) and thermally-induced nitrito-( $\eta^2$ -O,ON) (right) isomers in [Ni(*N,N'*-dipropyl-ethylenediamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] (Laskar *et al.*, 2001).

In 2011, we reported the first observation of both thermal- and photo-induced isomerism in the same system, for single crystals of the complex [Ni(Et<sub>4</sub>dien)( $\eta^2$ -O,ON)( $\eta^1$ -NO<sub>2</sub>)], where Et<sub>4</sub>dien = *N,N,N',N'*-tetraethyldiethylenetriamine (Hatcher *et al.*, 2011). The complex was designed to be similar to the well-studied [NiL<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] systems, however it differs by the inclusion of the tridentate amine group. Et<sub>4</sub>dien was again chosen as a bulky, photoinert ancillary fragment that should dominate the crystal packing. The complex is interesting as it already contains two differing nitrite arrangements in its GS structure, one monodentate and one nitrito-( $\eta^2$ -O,ON) group, adopting the bidentate arrangement in order to complete the octahedral coordination sphere (Figure 9). Nitrito-( $\eta^2$ -O,ON) is found to be inert to conversion under the conditions investigated, however the remaining monodentate group displays a variety of complicated isomerisation behaviour.



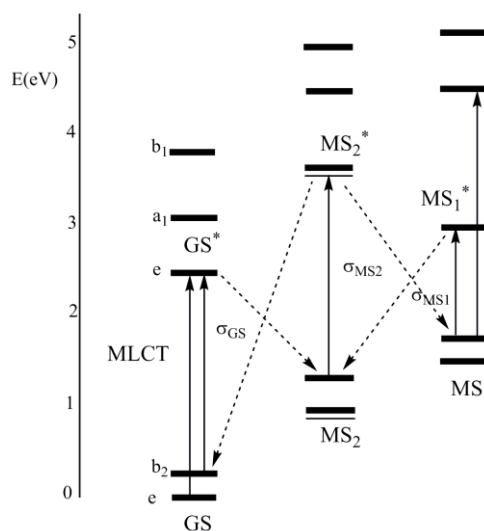
**Figure 9** Single crystal X-ray structures of the GS nitro-( $\eta^1$ -NO<sub>2</sub>) (left) and ES *endo*-nitrito-( $\eta^1$ -ONO) (right) isomers in [Ni(Et<sub>4</sub>dien)( $\eta^2$ -O,ON)( $\eta^1$ -NO<sub>2</sub>)] (Hatcher *et al.*, 2011).

Crystallising as a mixture of nitro-( $\eta^1$ -NO<sub>2</sub>) and *endo*-nitrito-( $\eta^1$ -ONO) isomers under ambient conditions, with occupancies of 78% and 22% respectively, this isomeric ratio is found to be entirely temperature dependent. While slow cooling below 160 K induces conversion to a clean, 100% nitro-( $\eta^1$ -NO<sub>2</sub>) arrangement, warming the system above 160 K promotes conversion to the *endo*-nitrito form, showing the isomers are subject to a thermodynamic equilibrium in the single crystal. A maximum thermal excitation of 42% *endo*-nitrito-( $\eta^1$ -ONO) is achieved at 370 K. At the same time, photoactivation of the clean, nitro-( $\eta^1$ -NO<sub>2</sub>) isomer at 100 K with 400 nm LED light induced 86% conversion to a photoactivated *endo*-nitrito-( $\eta^1$ -ONO) species that is confirmed to be metastable at low temperature. While no higher photoactivation level can be achieved with further irradiation at  $\lambda = 400$  nm, via a combination of single-crystal UV/vis spectroscopy and extensive photocrystallographic study it was later revealed that 100% photoconversion to the *endo*-nitrito form can be induced at  $\lambda = 500$  nm (Hatcher *et al.*, 2013). This result highlights how the absorption properties of the sample are particularly important in controlling the progress of the solid-state isomerisation, and again showcases how the combined information from complimentary spectroscopic and crystallographic techniques is invaluable to provide a complete picture of the solid-state system under study. [Ni(Et<sub>4</sub>dien)( $\eta^2$ -O,ON)( $\eta^1$ -NO<sub>2</sub>)] has also been the subject of pseudo-steady-state photocrystallographic studies, investigating photoisomerisation in the system at shorter timescales under continuous illumination (Hatcher *et al.*, 2013). Results have indicated the presence of a third monodentate *exo*-nitrito-( $\eta^1$ -ONO) arrangement that is only observable under pseudo-steady-state conditions and, as such, is believed to be a transient photoexcited linkage isomer. Detailed study of this system has shown that the linkage isomerism reaction in the single crystal is highly dependent on temperature, and highlights how closely both the thermal and photoinduced processes are related in these systems.

Nitro – nitrito isomerism has also been reported in systems containing different transition metal centres, including palladium (Bajwa *et al.*, 2012) and platinum species (Warren *et al.*, 2012). In the latter photocrystallographic study, the absorption properties of the sample are shown to be affected by the nature of the metal centre. Complimentary UV/vis and computational work are presented that indicate a shift to shorter wavelengths of higher energy is required for excitation in nitrite species containing heavier transition metals. Despite varying the excitation wavelength, photoactivation levels are reported to be lower in general for palladium and platinum species in comparison to the analogous nickel compounds. This indicates that first row transition metal complexes are most suitable for the design of systems to undergo maximal levels of photoconversion.

## 7. Electronic and Mechanistic Studies

Absorption properties are closely related to the electronic structure of a complex and, as such, there has been some interest in elucidating the electronic mechanism by which linkage isomer conversion proceeds in the single crystal. When an ES species is produced on the absorption of light, the process must be initiated by an optical electronic excitation. Detailed study of the electronic structure in complexes of the general formula  $ML_5NO$  have been conducted by Woike *et. al.*, leading them to propose a general pathway for the production of linkage isomers  $MS_1$  and  $MS_2$  (Schaniel & Woike, 2009). Although this work focusses on nitrosyl species, the authors expect their general pathway to be applicable to other ligands that show linkage isomer conversion.



**Figure 10.** Schematic diagram of the general pathway to the formation of metastable nitrosyl linkage isomers in  $ML_5NO$  complexes (Schaniel & Woike, 2009).

Their scheme, which is reproduced in Figure 10, suggests that conversion proceeds via metal-to-ligand-charge-transfer (MLCT), induced when photons of correct energy are absorbed by the complex. The authors outline two conditions that must be satisfied for photoisomerisation to occur. Firstly, excitation must promote electron transfer between two orbitals such that a change in the metal – nitrosyl bond is induced, *e.g.* MLCT via a  $d \rightarrow \pi^*(NO)$  transition. Secondly, for a metastable isomer to be generated the potential energy surface for the ES isomer must have a minimum point that directly overlaps a maximum point (or “saddle point”) on the GS energy surface. For nitrosyl isomers the authors identify two such points in their calculated data, corresponding to the production of  $MS_1$  and  $MS_2$ . The relative electronic populations in each state and their absorption cross sections at the excitation wavelength are also shown to be important, considering that transitions both to and from a particular electronic state might be induced at the same excitation wavelength. As such, the rate at

which the state is populated must exceed the rate of depopulation for there to be a detectable occupancy of the photoexcited isomer. This latter point provides an additional explanation for why a range of excitation levels can be observed in solid-state metastable linkage isomer species.

## 8. Conclusions

The purpose of this review article has been to emphasise the important contribution structural chemistry has to make in the study of small, photoswitchable species, in light of their potential to be applied to a number of significant real-world challenges. The discussion has outlined how a large volume of work has been dedicated to the study of linkage isomerism and, in particular, the development of reliable photocrystallographic methods has facilitated our growing understanding of the phenomenon in the single crystal. While significant steps have been taken towards explaining the key steric and electronic factors that can influence isomerisation, it is evident that further work is required to fully understand and predict the progress of these complicated solid-state transformations. There remain some key problems that must be overcome before these species might be suitable as real solid-state devices, including a need for the rational design of systems that will undergo fully controllable and reversible conversion under ambient conditions. While much of the work conducted to date relies on the use of single crystal X-ray methods to obtain a full, 3D picture of the changes, it is expected that in future there will be a requirement to analyse these photoswitchable species in their technologically applicable medium. It is likely that the functionality of these photoactive species may be best exploited in the form of powders, surfaces, gels or amorphous dispersions and, as such, a number of different diffraction techniques could be suitable for their characterisation. This review has additionally highlighted the benefits of combining crystallographic results with spectroscopic and computational studies, to obtain the most complete understanding possible of the solid-state transformation. This type of approach is likely to become even more vital as we move towards analysing compounds in ever more complicated solid-state forms, and it is expected that structural chemistry will continue to play a vital role in the future development of this exciting and diverse research area.

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